

pH Influence on the stability of foams with protein-polysaccharide complexes at their interfaces

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Food foams such as marshmallow, Chantilly and mousses have behavior and stability directly connected with their microstructure, bubble size distribution and interfacial properties. A high interfacial tension inherent to air/liquid foams interfaces affects its stability, and thus it has a direct impact on processing, storage and product handling. In this work, the interactions of egg albumin with various types of polysaccharides were investigated by drop tensiometry, interfacial rheology and foam stability. The progressive addition of egg albumin and polysaccharide in water induced a drop of the air–water surface tension which was dependent on the pH and polysaccharide type. At pH 4, that is below the isoelectric point of egg albumin ($pI = 4.5$) the surface tension was decreased from 70 mN/m to 42 mN/m by the presence of the protein, and from 70 mN/m to 43 mN/m, 40 mN/m and 38 mN/m by subsequent addition of xanthan, guar gum and κ -carrageenan, respectively. At pH 7.5 the surface tension was decreased from 70 mN/m to 43 mN/m by the simultaneous presence of the protein and κ -carrageenan. However, a higher surface tension of 48 and 50 mN/m was found when xanthan and guar gum were added, respectively, when compared with carrageenan addition. The main role on the stabilization of protein–polysaccharide stabilized interfaces was identified on the elasticity of the interface. Foam stability experiments confirmed that egg-albumin/ κ -carrageenan at pH below the protein isoelectric point are the most efficient systems to stabilize air/water interfaces. These results clearly indicate that protein-polysaccharide coacervation at the air/water interface is an efficient process to increase foam stability.

1. Introduction

Foams are complex systems which can be defined as products with a gaseous phase stabilized in a continuous matrix (Chang & Hartel, 2002). They constitute an important class of food materials (Mezzenga, Schurtenberger, Burbidge, & Michel, 2005) and various types of foams have been engineered to develop new products well adapted to consumer preferences, using air, as a zero cost ingredient (Campbell & Mougeot, 1999; Narchi, Vial, & Djelveh, 2009). Food foams such as ice cream, marshmallow, Chantilly and mousses, have their stability and behavior intimately related to their microstructure, and more precisely, to the air bubble size, distribution, volume fraction, etc. (Campbell & Mougeot, 1999; Müller-Fischer & Windhab, 2005). The other main parameter affecting the

stability of the foams is the air/water surface tension which has to be reduced by the use of suitable surfactants: high surface tension between the air phase and the liquid phase, being primarily responsible for poor processing, storage and handling of the final products (Kokini & Van Aken, 2006).

The rheological study of the interface in foams can determine how the dispersed phase resists to deformation, or even coalescence. The composition of interfacial layers alters the structure and rheology, being determinant for the shelf life study and the choice of the foaming agent (Grigoriev, Derkatch, Kragel, & Miller, 2007). The presence of a foaming agent affects both the properties of the gas–liquid interface, as well the viscosity of the interface and permeability of the film between phases (Dutta et al., 2002; Mezzenga, Folmer, & Hughes, 2004). The most commonly used macromolecular foaming agents in foods are proteins.

Polysaccharides, with gyration radii ranging between (10 Å a 1000 Å), can also be used to stabilize emulsions and foams by a different mechanism. Once dispersed in water they have the property to increase bulk viscosity and improve stability against coalescence. The most common polysaccharides used for

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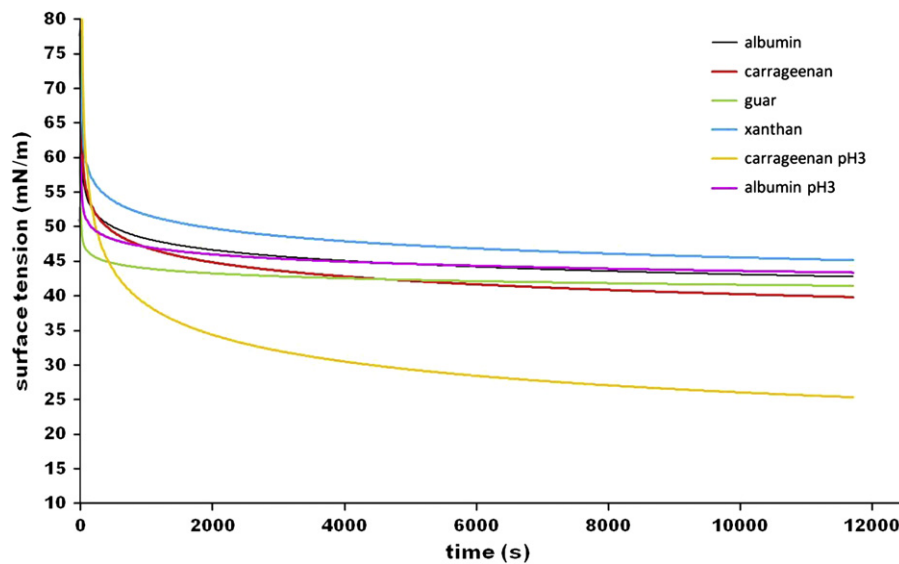


Fig. 1. Surface tension versus time as measured by pendant drop experiments in a solution containing albumin and albumin plus polysaccharides at acidic pH (4 and 3).

confectionary products are guar gum, xanthan gum and κ -carrageenan. (Lennox, 2002; Wei, Wang, & Wu, 2001). When mixed in presence of proteins they can interact with the latter by hydrophobic interactions, hydrogen bonding and electrostatic interactions, giving rise to a synergistic effect (Narchi et al., 2009).

Accordingly to Young, Kappel, and Bladt (2003), the addition of a polysaccharide increases the stability of products with high sugar content. Xanthan gum, for example, an exopolysaccharide with a high molecular weight (between 10^3 and 10^4 kDa), when present in solution in concentrations below 0.3%, only increases the viscosity, whereas beyond this value, strongly interacts with other sugar components altering the sugar solution properties (Fernandez, Martino, Zaritsky, Guignon, & Sanz, 2007; Wei et al., 2001). The behavior can be explained by the rigidity of the Xanthan chains and by the weakness of the network between macromolecules that involves hydrogen bonds. Unlike the guar gum, xanthan gum is carboxylated, negatively charged in the pH ranges typically used for

food, and can present electrostatic interactions with proteins at $\text{pH} > \text{pK}$ (Narchi et al., 2009).

The presence of guar gum in the system in concentrations between 0.15 and 0.5%, has been reported to contribute to the increase of bubbles' volume in food foams, by increasing elasticity and conferring a pseudo-solid behavior (Chavez-Montes, Choplin, & Schaer, 2007; Fernandez et al., 2007). Guar gum is neutral, with high molecular weights (about 10^3 kDa), and can be used as a bulk agent to increase viscosity, but does not generally lead to gel formation (Narchi et al., 2009).

Finally, κ -carrageenan, an anionic polysaccharides with linear chains with pendant galactose residues in position β -1,3 and α -1,4 (Singh, Tamehana, Hemar, & Munro, 2003), in the presence of other sugars and at concentrations as low as 0.05%, has been shown to produce a reticular structure, conferring to the system an improved stability (Yanes, Duran, & Costell, 2002). At larger concentration it is typically used as gelling agent.

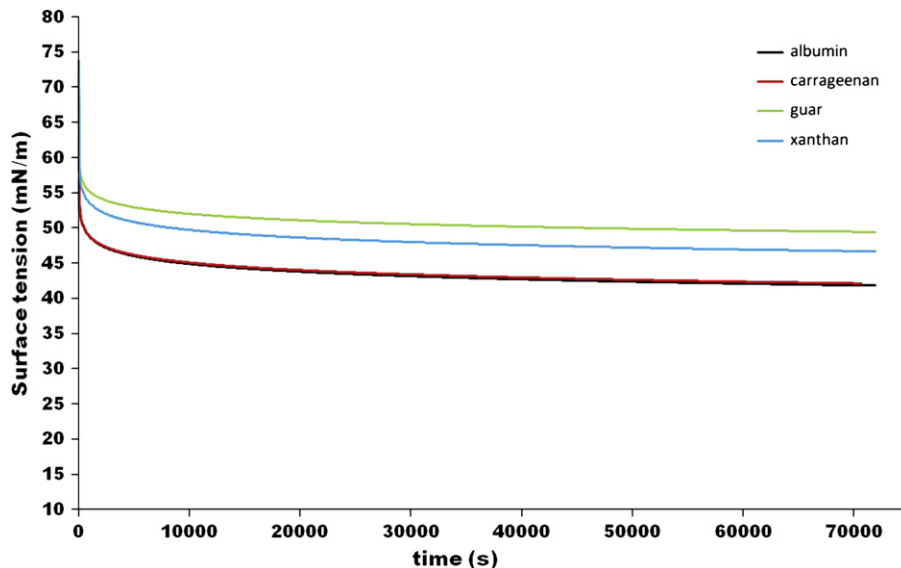


Fig. 2. Surface tension versus time as measured by pendant drop experiments in a solution containing albumin and albumin plus polysaccharides at pH 7.5.

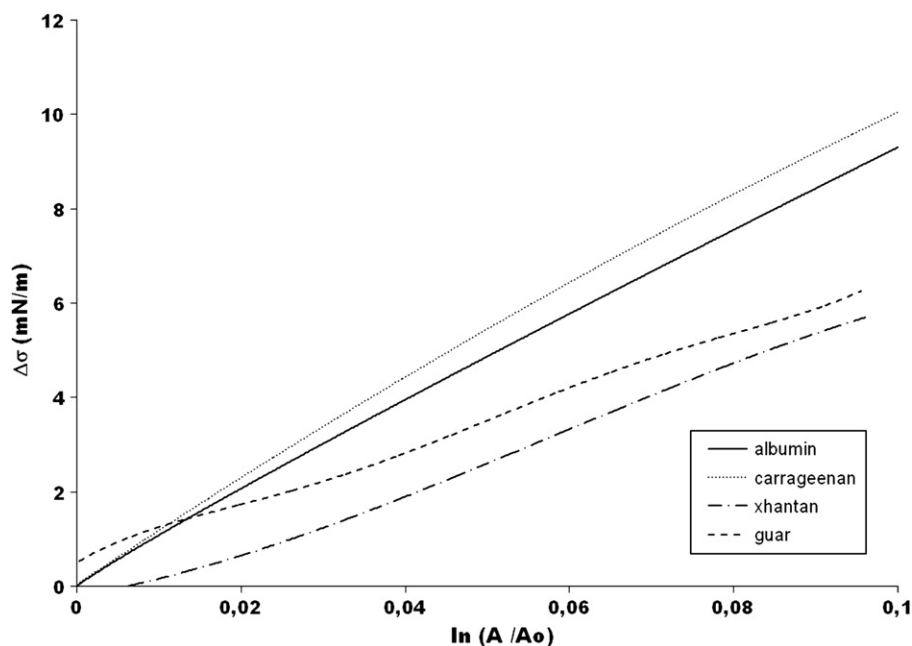


Fig. 3. Surface tension versus deformation of the bubble for samples containing albumin and albumin plus polysaccharide at pH 4.

Mixtures of oppositely charged proteins and polysaccharides have a tremendous relevance in foods because they offer a unique possibility to tune texture in gels and to stabilize surfaces and interfaces via electrostatic interactions, a process generally referred as coacervation (Onesippe & Lagerge, 2009). Furthermore, the electrostatic complexation of a protein with a polysaccharide can also provide a protective functionality, by preventing for example protein denaturation (Capitani, Perez, Pacheco, Teresa, & Pilosof, 2007). Generally, the performance of proteins alone in stabilizing foams can be improved by the addition of others stabilizing agents, usually polysaccharides (Narchi et al., 2009).

In order to improve foaming or foam stability, in their formulation, mousses or other protein-sugar systems such as marshmallow or meringues typically contain proteins, and most often albumin. Albumin is the main protein present in egg whites (Çelik,

Ylmaz, Isik, & Ustun, 2007; Foegeding, Luck, & Davis, 2006; Glaser, Paulson, Speers, Yada, & Rousseau, 2007; Müller-Fischer & Windhab, 2005; Raikos, Campbell, & Euston, 2007), out of more than forty different proteins, which illustrates well the capability of egg white to stabilize foams (Damodaran, Anand, & Razumovsky, 1998; Mleko, Kristinsson, Liang, & Gustaw, 2007).

The rheological properties of protein-polysaccharides coacervates have been already investigated in complex emulsified systems (Onesippe & Lagerge, 2009; Sperber, Schols, Stuart, Norde, & Voragen, 2009; Ye, 2008). Interfacial rheology studies of protein-polysaccharide monolayer, however, are more sparse in literature (Erni, Fischer, Herle, Haug, & Windhab, 2008; Turgeon, Schmitt, & Sanchez, 2007), although this method constitutes an indirect way to obtain valuable information about the interface stability (Murray, 2007).

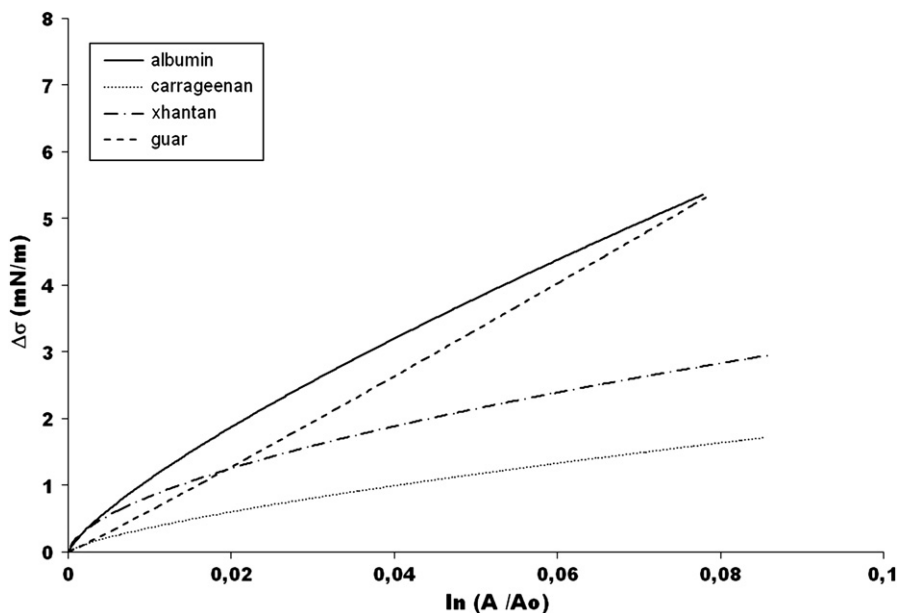


Fig. 4. Surface tension versus deformation of the bubble for samples containing albumin and albumin plus polysaccharide at pH 7.5.

The aim of the present work is to study the interfacial properties of a protein monolayer upon addition of various polysaccharides at different pHs conditions. Egg albumen was selected as model system for globular proteins, while both neutral and anionic polysaccharides at pHs below and above the isoelectric point of the protein were considered. The results on interfacial properties of the various protein-polysaccharide monolayer were then used to interpret the shelf life of real foams stabilized by corresponding systems.

2. Experimental section

2.1. Materials

All ingredients used were food grade and used as received: egg albumin was purchased from Prolabo (Switzerland), while xanthan gum (Ref: G1253), guar gum (Ref: G4129) and κ -carrageenan gum (Ref: 22 048) were purchased from Sigma Aldrich Inc, (Germany). Citric acid was used as agent for adjusting the pH of the water-protein-polysaccharide solutions.

2.2. Methods

2.2.1. pH determination

The values of pH for the study were selected to allow a negative-positive complexation of carrageenan-albumin pairs at acidic pH (3 and 4), while preventing the complexation of weak polyelectrolyte (xanthan) and neutral polysaccharides. A pH 7.5, on the other hand was also selected to allow only repulsive/hydrophobic interactions.

pH measurements were performed by direct immersion of the electrode in the sample at a controlled temperature of 20 °C by a pH meter model HD8602, from Delta Ohm.

2.2.2. Density determination

Density measurements were carried out for the determination of the surface tension via the fitting of the Laplacian profile of the droplet, which is the result of the balance between surface tension and gravity.

A density-meter model DMA 4500, from Anton Paar was used to performed density measurements of the solutions.

2.2.3. Interfacial tension

A drop tensiometer (I.T. Concept, France) was used to study the time-evolution of protein and polysaccharide adsorption at the interface via the pendant drop method. The tensiometer operates in volume-controlled regime, via continuous measurement of the drop area and volume, approximated by a Laplacian profile. Although larger drops increase the accuracy of measurements, the precision of interfacial tension measurements is practically limited by the maximum affordable size of the bubble which does not detach from the needle by negative gravity effects (Archimede's principle). In the present case, the mean average area was of 8 mm², with cyclic periodic oscillation of amplitude of 0.5 mm² for oscillatory analysis. The analyses were performed at both pH 4 and pH

Table 1

Values of surface tension (σ), interfacial dilatational modulus (Ed) and their Ed/ σ ratio for samples at pH 7.5.

Sample pH 7.5	σ (mN/m)	Ed (mN/m)	Ed/ σ
albumin	43	60,75	1413
carrageenan	43	32,19	0.749
xanthan	48	50,44	1073
guar	50	81,50	1630

7.5 in solutions containing 1.5% albumin, with or without the additional 0.15% of the various polysaccharides considered.

2.2.4. Bulk shear rheology

In order to determine the linear viscoelastic region of the bulk system, amplitude sweep experiments were performed with constant frequency of 1 Hz and deformation varying from 0.1 to 10%; G' and G'' were successively analyzed at constant deformation of 0.3% sweeping the frequency between 0.1 and 10 Hz. The measurements were performed on the samples containing albumin and albumin plus polysaccharide, for pH 4 and pH 7.5. A cone plate geometry \varnothing 50 mm, and $\theta = 1^\circ$ was used, while temperature was maintained fixed at 20 °C by a Peltier system. A Physica Anton Paar MCR500 rheometer was used for the measurements.

Bulk rheology measurements were used to validate the interfacial rheology study via the Bussinesq Number check (see below for more details).

2.2.5. Interfacial shear rheology

An interfacial rheology cell (IRC) and a Bicone sensor, \varnothing 68 mm, $\theta = 5^\circ$ were used for interfacial shear rheology. Identical strain sweep experiments were performed to identify the linear viscoelastic regime, and frequency sweeps between 0.1 and 10 Hz were also performed. In order to validate the interfacial rheometry measurement, the Bussinesq Number was evaluated for each individual measurement, following the methodology described by [Erni, Fischer, and Windhab \(2005\)](#). Besides the amplitude and frequency sweep, an additional test was performed in two steps: a constant deformation of 10%, well beyond the linear viscoelastic region was applied for 10 min, followed by a constant deformation of 0.3% in the linear viscoelastic region for 1 h. G' and G'' were followed as a function of time to determine how the interface viscoelastic properties evolved. A Physica Anton Paar MCR500 rheometer was used for the measurements.

2.2.6. Foam stability

All the nine solutions were prepared in a graduated beaker of 200 ml and a volume of 10 ml was transferred to another graduated beaker of 50 ml. The beaker was covered with a paraffin film and stirred vigorously at 800 rpm for 2 min by a magnetic stirrer. The foam stability was analyzed as a function of time observing the volume of foam formed after stirring.

2.2.7. Sample preparation

1.5 g of albumin from egg whites was added in a beaker containing 100 g of distilled water. The solution was mixed with a stirred magnetic plate. To the albumin solution 0.15 g of polysaccharide were added and further stirred for the time needed to homogenize the solution. For studies in weak base environment, the pH was measured and adjusted for all solutions to 7.5. For studies in acidic environment, citric acid was added to the albumin solution and the pH adjusted to 4 and 3. In both basic and acidic conditions, the various polysaccharides were added afterwards. All the ingredients were added considering mass basis.

Table 2

Values of surface tension (σ), interfacial dilatational modulus (Ed) and their Ed/ σ ratio for samples at pH 4 and 3 (albumin and carrageenan gum).

Sample pH4	σ (mN/m)	Ed(mN/m)	Ed/ σ
albumin	42	78,08	1735
carrageenan	38	75,58	2290
xanthan	43	33,93	0.771
guar	40	56,94	1582
carrageenan pH3	24	190,73	7336
albumin pH3	42	46,22	1100

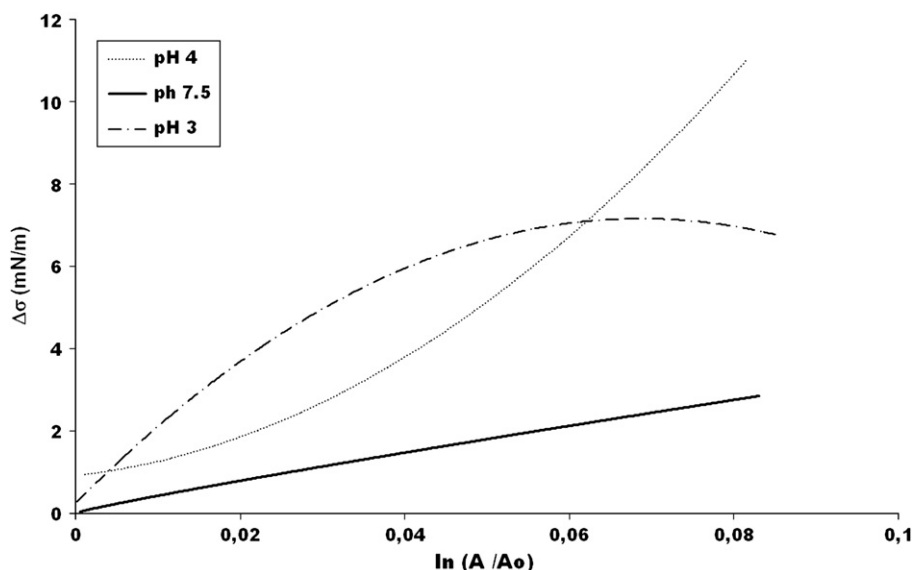


Fig. 5. Surface tension versus deformation of the bubble for samples containing albumin plus carrageenan gum at pH 7.5, 4 and 3.

3. Results and discussion

Fig. 1 illustrates the evolution of the air–water surface tension versus time measured by drop tensiometer for the albumin solution and the albumin solution in presence of the various polysaccharides in acidic conditions. While xanthan leads to a moderate increase in surface tension, carrageenan and guar gum both contribute to a decrease of the overall surface tension, with carrageenan giving the stronger decrease. In the figure it is also shown the evolution of surface tension by further reducing the pH to 3 in the case of carrageenan: the plateau value of surface tension decreases to a value as low as 26 mN/m. Because the isoelectric point (IP) of the albumin is 4.5, at both pH 4 and 3 the protein is positively charged, guar gum is neutral and xanthan is nearly entirely protonated ($\text{pH} < \text{pK} = 4.8$) and thus, also essentially neutral (Garti & Benichou, 2004); being carrageenan the only negatively charged polysaccharide. Since the number of positive residues in the protein increases with decreasing pH, also the electrostatic interactions between carrageenan and albumin are expected to be increased by lowering pH; thus, the decrease in surface tension is likely to be greatly affected by the formation of coacervates between proteins and polysaccharides. The presence of

coacervates in the system contribute to interface rigidity rather than on the interfacial tension.

As a further confirmation that electrostatic interactions play a major role on the establishment of surface properties, Fig. 2 shows the same time-evolution for surface tension stabilized by the same protein–polysaccharide systems, this time at pH of 7.5, where the protein is negatively charged and the carrageenan, xanthan, and guar gum are respectively negatively, negatively and neutrally charged. Thus at this conditions, repulsive interactions, hydrophobic interactions and hydrogen bonding interactions are the only possible types of interactions for the protein and the polysaccharides, whereas attractive electrostatic interactions are inhibited. The resulting plateau moduli of the surface tension is either unaffected by the presence of the polysaccharide (for the carrageenan case), or even increased (xanthan and guar gum).

An additional insight on the interfacial properties of the protein/polysaccharide systems can be gained by comparing the interfacial elasticity of the interfaces obtained under different conditions. This is expressed by the interfacial dilatational modulus as (Lucassen-Reynders, 1981, chaps. 5–6).

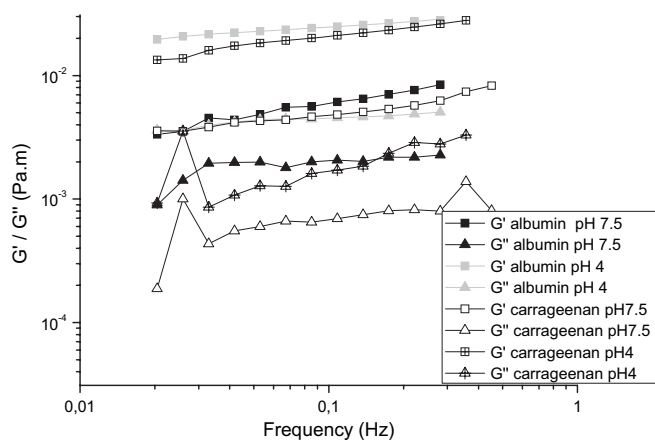


Fig. 6. G' and G'' values for the frequency sweep at the interface stabilized by protein–carrageenan mixtures at pHs 7.5 and 4.

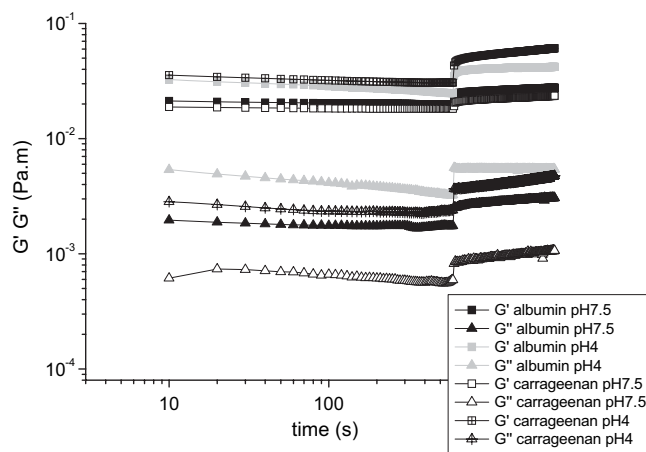


Fig. 7. G' and G'' as a function of time at the water–air interface for samples containing albumin and albumin plus polysaccharide at pH 4 and 7.5 after a two-step deformation process.

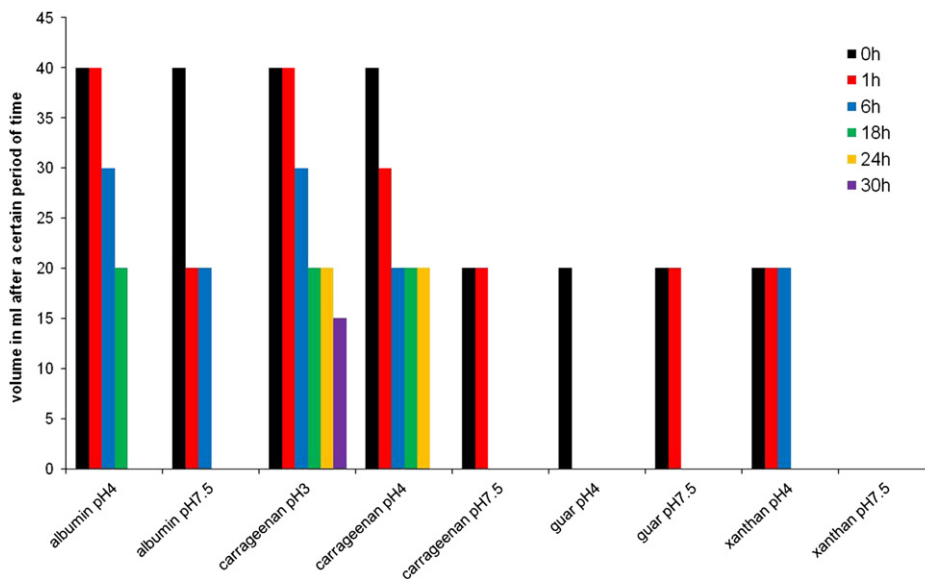


Fig. 8. Foam stability study versus time for different albumin/polysaccharides solutions at pHs 7.5, 4 and 3.

$$E_D = \frac{d\sigma}{d(\ln A)} \quad (1)$$

where σ is the surface tension and A the instant area of the interface. Thus, in a volume expansion experiment, the interfacial elasticity can be extracted by the slope of the increase of surface tension versus deformation ϵ_D with

$$\epsilon_D = \ln(A/A_0) \quad (2)$$

The interfacial elasticity value can be used to predict the stability of interface against Ostwald Ripening using the Gibbs criterion, which states that interfaces are stable when (Lucassen-Reynders, 1981, chaps. 5–6).

$$E_D/\sigma > 1/2 \quad (3)$$

Figs. 3 and 4 gives the $\Delta\sigma$ vs ϵ_D curves for the albumin–polysaccharide systems at pH4 and 7.5, respectively, from which the interfacial elasticity E_D can be extracted, and results on σ , E_D and their ratio are summarized for the various cases considered in Tables 1 and 2. Clearly, when attractive electrostatic interactions are suppressed (Fig. 4, and Table 1), the surface tension is either unaffected or increased by the presence of the polysaccharide, and the elasticity either decreased or increased, as in the case of guar, which however also experiences increases in the surface tension. As a result, the Gibbs ratio against disproportionation has values in between 0.75 and 1.6, which imply moderate, yet favorable stability. When the pH is, however, decreased to 4 (Fig. 3, and Table 2), and the electrostatic attractive interactions are induced in the case of carrageenan, the ratios reaches a value of 2.3, inferring increased stability. Fig. 5 and Table 2 also compare the dependence of elasticity of albumin–carrageenan as a function of pH by further decreasing the pH to 3 and thus enhancing electrostatic attraction. A remarkable increase in E_D is observed (190 mN/m), together with a sharp decrease of the surface tension (26 mN/m) leading to a Gibbs ratio as high as 7.3. These results suggest that coacervate-stabilized foam interfaces should be very stable against Ostwald ripening, as a result of cross-linked-like interfaces (Ruíz-Henestrosa, Sánchez, & Patino, 2008). A similar approach has been used recently to assess the stability of oil–water interfaces stabilized by

a cross-linked protein monolayer (Romoscanu & Mezzenga, 2005 and Romoscanu & Mezzenga, 2006).

As can be observed by all the oscillatory test experiments, both $\Delta\sigma$ and E_D considerably deviate from a linear behavior with dilatation of the bubble droplet. This effect, which is similar to that observed by Romoscanu and Mezzenga (2005) for cross-linked protein monolayer, can be attributed to the presence of strongly buried and interacting interfaces, as expected in protein–polysaccharide mixtures.

Oscillatory interfacial rheometry provided additional information on the strength of the interfaces in the systems considered.

Fig. 6 illustrates the frequency sweep for the samples containing 1.5% of albumin and 0.15% of carrageenan at pH 4 and 7.5. Both scans show that the interface is viscoelastic, with G' larger than G'' by about one order of magnitude: this is consistent with an interfacial rubbery behavior; nonetheless, in the case of pH4, both G' and G'' are increased compared to the pH7 case, as a result of increased physical interactions between the protein and the carrageenan. In particular Fig. 6 shows that the increase in the gap between G' and G'' appears when carrageenan is added to the system, reinforcing the statement that the interactions between the polysaccharide and the protein increase the interfacial rigidity.

It is interesting to study how the interfacial behavior evolves when the interface is subjected to the following deformation protocol (i): first a constant deformation of 10%, well beyond the linear viscoelastic region is applied for 10 min and then (ii) a constant deformation of 0.3% in the linear viscoelastic region is maintained for 1 h (Fig. 7).

When a deformation above the viscoelastic region is applied ($\gamma = 10\%$) a decrease of both G' and G'' occurs in each individual samples, possibly due to perturbations on the optimal packing of the various macromolecules at the interface. When the large deformation is released, however, and a lower deformation applied ($\gamma = 0.3\%$) both storage and loss moduli recover back the original value, in agreement with recently reported results (Krishnaswamy, Majumdar, & Sood, 2007). Interestingly, however, at pH 4 the system containing carrageenan increase both G' and G'' to values beyond their pristine values. A tentative explanation for this phenomenon is that the two-step creep experiment favors an improved molecular packing of the coacervate at the interface,

leading to superior interfacial properties (Baeza, Pilosof, Sanchez, & Patino, 2006; Lorenzo, Zaritzky, & Califano, 2008; Wierenga, Kosters, Egmond, Voragen, & De Jongh, 2006). More extended studies are, however, needed to fully assess this point.

We note that all interfacial experiments (dilatation and shear) were produced in double set, each set being indistinguishable, which guarantees reproducibility of the results presented.

In order to determine whether the interfacial study gives a comprehensive insight on the stability of foams based on homologue formulations, time-stability experiments of foams stabilized by identical polysaccharide–protein mixture was studied.

The volume of foams formed in the beaker was observed after sample preparation as a function of time for the various albumin/polysaccharide formulations, as shown in Fig. 8. For the solutions containing 1.5% of albumin at both pH 7.5 and 4, the volume observed straight after the foaming process was of 40 ml; identical trends were observed for the solutions containing 1.5% of albumin and 0.15% of carrageenan at either pH 4 or 3. For the other solutions prepared with 0.15% of xanthan gum (pH 4), guar gum (pH 7.5 and 4) and carrageenan at pH 7.5, however, a reduced foam volume of 20 ml was observed immediately after foaming. For the solution containing xanthan gum at pH 7.5 there was no foam formation observed and the 10 ml of solution remained, unfoamed, in the beaker. After 1 h the foam could not be longer observed in the solution of guar gum at pH 4. After 18 h 20 ml foam remained only in the beaker containing the following solutions: 1.5% albumin at pH 4, 1.5% albumin and 0.15% carrageenan at pH 4 and 3. After 24 h the foam could be observed (20 ml) only in the solutions containing carrageenan at pH 4 and 3. After 30 h residual foam could be observed only for the carrageenan solution at pH 3.

Therefore, although individual foam cases follows specific kinetics in the decrease of the foams volume, the long-term foam stability is clearly correlated with the air–water interfacial properties, mediated by the protein–polysaccharide complexes. In summary, the macroscopic time-dependent volume evolution of the foam directly corroborates with results from surface tension and interfacial rheology, demonstrating that carrageenan addition at pH below the isoelectric point of albumin can greatly improve foam stability, via coacervates formation.

4. Conclusions

We have used drop tensiometry and interfacial shear rheology to investigate the properties of the air–water interface stabilized by egg albumin–polysaccharides mixtures at various pHs. The results have then been compared with the macroscopic behavior of foams stabilized by identical protein/polysaccharide mixtures at identical pHs, expressed by the time-dependent volume of the foam. The main finding of the present study is that using pH conditions and protein–polysaccharide pairs capable to undergo ionic coacervation, is a robust protocol to stabilize air–water interfaces and the corresponding foams. For a given coacervate pair, the stability of the interface is directly dependent on the amount of ionic interactions between protein and polysaccharide. Finally, the difference between pH 3 and pH 4 arises from the increased coacervation between carrageenan and protein as the result of increased positive charge of the albumin. Indeed, while at pH 4 the protein is very near to the PI (4.5) so the overall charge is only weakly positive, a drop of pH to 3 induces a deep increase in positive charges in the protein with only minor changes in the negative charge distribution of the carrageenan, being this latter a strongly acidic polysaccharide, leading to a more efficient charge complexation.

These findings can be exploited to better engineer and improve the foam stability in real products such as ice cream, marshmallow, Chantilly, mousses, etc.

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